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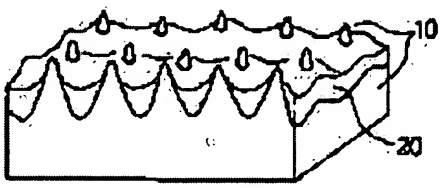
(54) SURFACE TREATING METHOD FOR FUEL BATTERY ELECTROLYTE FILM

(57)Abstract:

PURPOSE: To provide a fuel battery electrolyte film having an enlarged field of reaction by sputtering of metal after surface roughening is carried out, thermal damage attributable to the surface treatment being able to be made small while entry of impurity is able to be prevented, highly precise control being able to be made of the composition of an alloy if the metal is such an alloy.

CONSTITUTION: The surface of a fuel battery ion conductive polymer 10 is subjected, by plasma etching, to surface roughening treatment, after which sputtering of metal is conducted to cause laminating of a metal layer 20 on the ion conductive polymer surface. In this way, the surface treatment of the ion conductive polymer is carried out.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the layered product which the metal layer deposited on the electrolyte membrane which has irregularity in the surface treatment approach of the electrolyte membrane for fuel cells, and a front face.
[0002]
[Description of the Prior Art] A fuel cell comes to carry out the laminating of the unit cell which generally consists of the anode and cathode which were formed in an electrolyte membrane and its both sides through a separator. In order to make it the oxidation reduction reaction of fuel gas and oxidant gas occur on each electrolyte membrane, the slot for passage of each gas is formed in each separator.
[0003] Reactant gas consists of fuel gas and oxidant gas, fuel gas is supplied to the anode side passage slot on the separator, and, on the other hand, oxidant gas is supplied to the passage slot of the separator by the side of a cathode. As a result of such supply of reactant gas, an electron is generated with advance of an electrochemical reaction and electrical energy is generated by taking out this electron from an external circuit.
[0004] The thing which forms an electrolyte membrane by ion conductive polymers, such as ion exchange membrane, and comes to form an electrode catalyst bed on it as such a fuel cell can be considered. In this case, an electrode catalyst bed is formed by the spray method, the applying method, hot pressing, plating, etc. Moreover, after carrying out surface treatment by plasma etching, the approach of performing electroless deposition, the method of pouring ion into an electrolyte membrane directly, etc. are proposed.
[0005] However, when an electrode catalyst bed is directly formed in an electrolyte membrane without surface roughening processing by the hotpress, plating, etc., since the front face is smooth, reaction scene products, such as oxidation reduction, are small. Although the approach of carrying out electroless deposition is also proposed after carrying out plasma etching of the front face in order to improve this, there is a possibility that a foreign matter may adhere to a front face in the process in which it moves from etching to plating.
[0006] Moreover, by the approach of an ion implantation, in order to make ion with the big mass of Pt ion etc. collide with an electrolyte membrane, the thermal damage done to an electrolyte membrane is serious, and cooling is needed. Moreover, it is [whether it alloys and or not] a question even if it pours in two or more sorts of ion by this approach.
[0007]
[Problem(s) to be Solved by the Invention] It is made against the background of the above Prior arts, expansion of a reaction place is enabled by surface roughening of an electrolyte membrane, and mixing of an impurity is prevented, and this invention does not have a thermal damage, and the layered product which the metal layer deposited on the electrolyte membrane which has two or more irregularity in the surface treatment approach and front faces which can presentation control an alloy, such as Pt alloy, is offered.
[0008]
[Means for Solving the Problem] This invention offers the layered product characterized by what the metal layer deposited on the electrolyte membrane which has two or more crevices and heights on the surface treatment approach of the electrolyte membrane for fuel cells characterized by making a metal layer deposit on the electrolyte membrane front face by which surface roughening was carried out by carrying out the spatter of the metal, and a front face, after performing surface roughening processing on the surface of an electrolyte membrane.
[0009] In this invention, as an electrolyte membrane, if an ion conductive polymer is used, it is effective. As this ion conductive polymer, a polyperfluoro sulfo nick acid [for example, Nafion 117 (the Du Pont make, cation exchange membrane)] etc. is desirable. Moreover, the thickness of an electrolyte membrane is about 50-200 micrometers about.
[0010] In this invention, as the approach of surface roughening, although approaches, such as plasma etching and sandblasting, are mentioned, it is plasma etching preferably.

[0011] Said plasma etching exposes an electrolyte membrane to the discharge which impresses a direct current or an alternating current and is maintained under the ambient atmosphere of low-pressure gas inter-electrode, and should just perform it by processing a front face continuously by various activity particles generated by discharge, such as an electron and ion.
[0012] The gas pressure in said plasma-etching processor is 3x10-3 - 5x10-3Torr preferably 1x10-3 to 1x10 to 2 Torr. As an ambient atmosphere in a processor, inorganic gas, such as an argon, nitrogen, and oxygen, these mixed gas, etc. are mentioned. Moreover, 0.1-1kV of applied voltage is desirable. Moreover, about the processing time, 3 - 90 minutes is desirable. In addition, about applied voltage and the processing time, the inclination for a front face to become coarse is shown, so that the front face of a processed material (electrolyte membrane) becomes coarse, so that applied voltage becomes large, and the processing time becomes long. Compared with the well-known ion implantation mentioned above, plasma etching using such argon ion, nitrogen ion, etc. has a small thermal damage, does not have the need for cooling, and is the desirable roughening approach.
[0013] Thus, after roughening a front face, the spatter of the metal is carried out to the front face after processing, and a metal is made to deposit on it. As this metal that carries out a spatter, the alloy containing platinum or platinum is desirable. As a metal used as platinum and an alloy, palladium, a rubidium, a ruthenium, titanium, chromium, cobalt, etc. are mentioned.
[0014] As the approach of said spatter processing, the target made from a metal (for example, the metaled duality or the plural metals which are used as platinum or platinum, and an alloy) is manufactured beforehand. The target of two sheets with which the approach of forming a metal layer with a conventional method using this differs from the quality of the material (-- for example, one side -- platinum and another side -- palladium, a rubidium, a ruthenium, titanium, chromium, cobalt, etc. --) -- by making it face, arranging, and impressing and carrying out the spatter of the electrical potential difference different, respectively to each target The so-called opposite target type alloy spatter which forms the alloy layer of a predetermined presentation ratio in an electrolyte membrane front face is mentioned.
[0015] It is not necessary to manufacture the target made from an alloy beforehand, and the spatter layer of an alloy can be directly manufactured by using an opposite target type alloy spatter. In addition, about a presentation ratio, by making it fluctuate according to an individual, respectively, and adjusting the electrical potential difference impressed to the target of two sheets with which the quality of the materials differ, it can consider as a desired thing, and accurate presentation control is possible and the high alloy layer of catalytic activity can be formed. For example, what is necessary is just to make into about abbreviation 7:10 the ratio of the electrical potential difference impressed to the target of platinum, and the target of Ti, when it is going to obtain the layer of the alloy of Pt3 Ti from platinum and titanium.
[0016] The coating weight of such a spatter layer is 0.04 - 2.0 mg/cm2. Usually it considers as extent.
[0017] In addition, in this invention, if a sputtering system with an etching function is used, the same equipment can perform, etching and a spatter continue with a vacuum, and can shift to actuation of a spatter from etching, and mixing of an impurity can be prevented.
[0018] Moreover, plasma etching using argon ion, nitrogen ion, etc. has a small thermal damage compared with the above-mentioned ion implantation, and since the plasma does not irradiate an electrolyte membrane at the time of sputtering, sputtering by the opposite target type sputtering system does not almost have a thermal damage, and does not have the need for cooling through both processes.
[0019] Thus, the layered product which the metal layer deposited on the electrolyte membrane which has two or more crevices and heights is obtained by carrying out surface roughening and carrying out the spatter of the metal. In here, the metal layer was stuck on the surface of the electrolyte membrane, and is deposited. Since surface roughening is made and detailed irregularity forms this in a front face, it is for the adhesive strength of an electrolyte membrane and a metal to improve.
[0020]
[Function] The ****** type perspective view of the layered product of this invention which the spatter of the metal was carried out [layered product] to drawing 1 , and made this film deposit further on it the ****** type perspective view of the electrolyte membrane in which surface roughening was carried out by plasma etching was shown in drawing 2 . In here, 10 is an electrolyte membrane and 20 is a metal.
[0021] Thus, by carrying out plasma etching, two or more irregularity is formed in a front face, surface area increases by that cause, the catalyst of platinum etc. deposits there, a crevice is entered, and the reaction place of oxidation reduction is expanded effectively. Reaction places are metal catalysts, such as platinum of an electrolyte membrane, and the three-phase zone of gas, and it means that a reaction place was not expanded without a metal entering to the back of HIDA of the irregularity of an electrolyte membrane.
[0022] Such a situation is shown in drawing 3 . Drawing 3 is the sectional view of drawing 2 R> 2. Since the front face of an electrolyte membrane has oxygen permeability slightly, it turns out that the surface phase 30 became a reaction

place altogether, and this is expanded. If it is the case of a cathode, the reaction of O(1/2)2+2H++2e-->H2 O occurs here.
[0023] Thus, by surface roughening and the metal spatter, the reaction place was expanded, i.e., the layered product which effective area expanded to appearance area is obtained.
[0024]
[Example] An example is given to below and this invention is further explained to a detail. In addition, this invention is not restrained by this example.
[0025] Ar plasma-etching processing during 30 minutes was performed in injection power 20W with the sputtering system to the 10cmx10cm film (175 micrometers in thickness) of example 1 Nafion 117 (Du Pont make). Then, applied voltage is adjusted so that a Pt3 Ti particle may deposit one target by setting the target of Pt and another side to Ti by the opposite target type alloy spatter, and it is 0.2 mg/cm2. Spatter processing was performed until it became thickness, and the cathode electrode catalyst bed for ion-exchange-membrane mold fuel cells was obtained.
[0026] Thus, in the obtained electrode catalyst bed, a reaction place is expanded, it becomes possible to advance the oxygen reduction reaction of a cathode for whether being Sumiya, and improvement in the fuel cell generation-of-electrical-energy engine performance can be aimed at by reducing electrical-potential-difference loss (cathode overvoltage) with a cathode by this. The current of the fuel cell using this electrode catalyst bed and the relation of an electrical potential difference are shown in drawing 4 .
The electrode catalyst bed was obtained like the example 1 except not carrying out example of comparison 1 plasma-etching processing. The current of the fuel cell using this electrode catalyst bed and the relation of an electrical potential difference are shown in drawing 4 .
[0027]
[Effect of the Invention] According to the approach of this invention, by roughening the front face of an electrolyte membrane and making a metal deposit further, the reaction place was expanded, i.e., the electrolyte membrane metal layered product which effective area expanded can be obtained to appearance area. Moreover, the approach of this invention can also prevent mixing of an impurity, if a thermal damage is small, performs surface roughening by plasma etching and performs a spatter with the same equipment. Moreover, if an opposite target type alloy spatter is used, since presentation control of an alloy can carry out with a sufficient precision, the high alloy phase of catalytic activity can be formed.

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* NOTICES *

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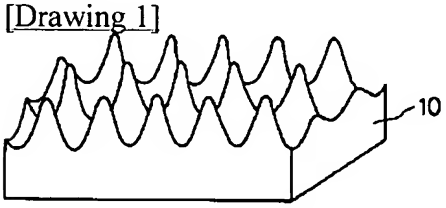
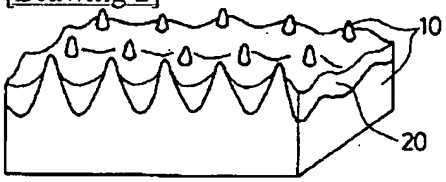
DRAWINGS

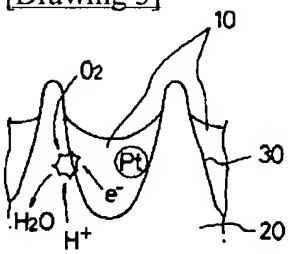
[Drawing 1]



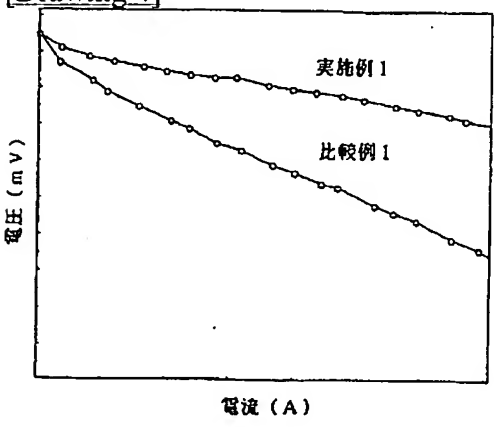
[Drawing 2]



[Drawing 3]



[Drawing 4]



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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the ****** type perspective view of the electrolyte membrane in which surface roughening was carried out by plasma etching.
[Drawing 2] It is the ****** type perspective view of the layered product of this invention which the metal deposited on the electrolyte membrane by which surface roughening was carried out.
[Drawing 3] It is the sectional view of drawing 2 .
[Drawing 4] It is the graph which shows the current of the fuel cell using the electrode catalyst bed obtained in the example 1 and the example 1 of a comparison, and the relation of an electrical potential difference.
[Description of Notations]
10 Electrolyte Membrane
20 Metal

[Translation done.]